



Enhanced *In Situ* Bioremediation Technologies

**July 16, 2002
NJDEP Public Hearing Room**

Sponsors: NJDEP & ITRC



- 1:00 - 1:05 Welcome**
Brian Sogorka, NJDEP Remediation Technology Manager
- 1:05 - 1:15 Keynote**
Evan Van Hook, NJDEP-SRP Assistant Commissioner
- 1:15 - 1:25 ITRC Update**
Marybeth Brenner, NJDEP-ITRC Point of Contact
- 1:25 - 3:45 Technical Program**
Andrew Marinucci, Ph.D., NJDEP, Moderator
- 1:25 - 2:05 Principles and Application in the Enhancement of in situ
reductive Dechlorination**
David Ellis, Ph.D., DuPont Corporation
- 2:05 - 2:45 Use of Edible Oil Emulsions to Support
in Situ Reductive Dechlorination.**
Michael Lee, Vice-President, Terra Systems, Inc.
- 2:45 - 3:00 Break**
- 3:00 - 3:40 Combined Chemical and Biological Strategies for
Remediation of Persistent PAH Contaminants
and Their Effects on Biodegradation.**
Jerome Kukor, Ph.D., and Pamela Sheehan
Biotechnology Center for Agriculture and the Environment
Rutgers University
- 3:40 - 3:45 Wrap-up**

Purpose of ITRC

ITRC is a state-led, national coalition of regulators and others working to







- * improve state permitting processes
- * speed implementation of new environmental technologies.



Goals

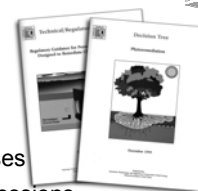
- * Achieve better environmental protection through innovative technologies
- * Reduce the technical/regulatory barriers to the use of new environmental technologies
- * Build confidence about using new technologies

Other Participants

- Industry representatives
- Academia
- Public stakeholders
- Federal agencies
 -  U.S. Department of Energy
 -  U.S. Environmental Protection Agency
 -  U.S. Department of Defense
- Host organization
 -  Environmental Council of the States
- State organizations
 -  Western Governors' Association
 -  Southern States Energy Board

Products & Services

- * Regulatory and Technical Guidelines
- * Technology Overviews
- * Case Studies
- * Peer Exchange
- * Technology Advocates
- * Classroom Training Courses
- * Internet-Based Training Sessions



Benefits to States

- * Access to peers and experts in other regulatory agencies
- * Shortened learning curve by obtaining advance knowledge of new and used technologies
- * Cost-effective involvement in demonstrations conducted in other jurisdictions
- * Sounding board for problem solving
- * Information and technology transfer
- * Maximize limited resources
- * Personal and professional development

Benefits to Industry

- * Forum conducive to advancing technology and solutions
- * Insight into the regulatory world
- * Access to multiple state entities
- * Opportunity for broader review of technology
- * Unique and cost-effective approach to demonstration and deployment of new technology
- * Mechanism to identify and integrate regulatory performance expectations amongst states

ITRC Contacts

Web Site: <http://www.itrcweb.org>

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Program Director:
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Technical Program

Andrew Marinucci, Ph.D.,
NJDEP, Moderator

**Principles and Application in the Enhancement of
in situ reductive Dechlorination**

David Ellis, Ph.D., DuPont Corporation

**Use of Edible Oil Emulsions to Support *in Situ* Reductive
Dechlorination.**

Michael Lee,
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**Combined Chemical and Biological Strategies for Remediation
of Persistent PAH Contaminants and
Their Effects on Biodegradation.**

Jerome Kukor, Ph.D., and Pamela Sheehan
Biotechnology Center for Agriculture and the Environment
Rutgers University

Principles and Applications of Enhanced In-Situ Reductive Dechlorination

David E. Ellis Ph.D.
DuPont Engineering - CRG

Presentation Outline

- Biodegradation mechanisms for chlorinated solvents
- Basic types of biotreatment systems
- The impacts of stoichiometry and hydrogeology on treatment system design
- RTDF's field pilot at Dover AFB
- Data quality evaluation

Common Chlorinated Solvents

- ♦ PCE: tetrachloroethene (C_2Cl_4)
- ♦ TCE: trichloroethene (C_2HCl_3)
- ♦ TCA: 1,1,1-trichloroethane ($C_2H_3Cl_3$) **
- ♦ 1,2-DCA: 1,2-dichloroethane ($C_2H_4Cl_2$) **
- ♦ CT: carbon tetrachloride (CCl_4)
- ♦ CF: chloroform ($CHCl_3$)
- ♦ DCM: dichloromethane (CH_2Cl_2) **
- ♦ HCB: hexachlorobenzene (C_6Cl_6)

** Normally biodegrades via another process

Why Choose Bioremediation?

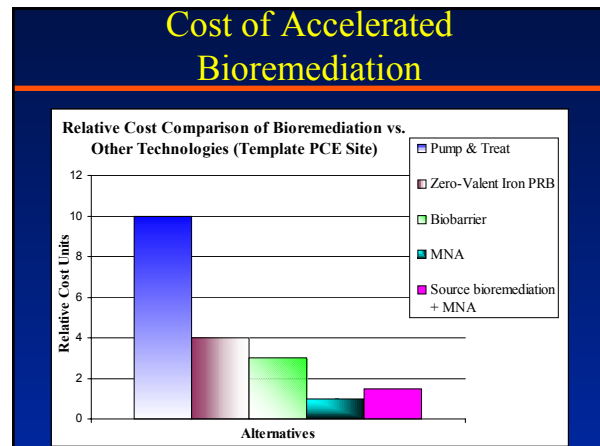
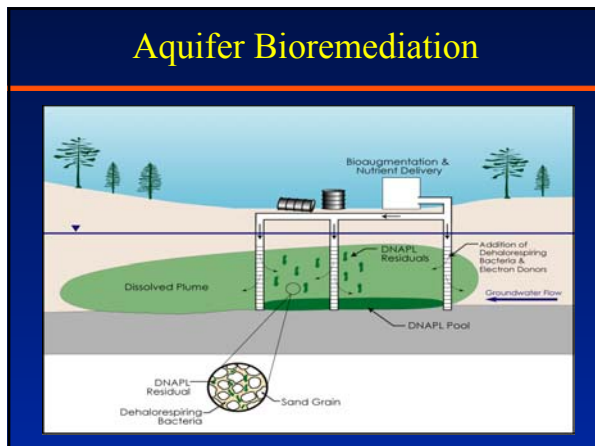
- ♦ Chlorinated solvents can biodegrade
- ♦ Biodegradation can accelerate dissolution and reduce cleanup time
- ♦ Cleanup occurs in place; contaminants are not transferred in location or phase
- ♦ May be a cheaper alternative

Accelerated Bioremediation Applications

- ♦ Groundwater plumes
 - Permeable bio-barriers (migration control)
 - Plume treatment (depends on size/cost)
- ♦ Source areas
 - Migration control or source treatment
 - Bioaugmentation
- ♦ Vadose zone
 - Bioventing or co-metabolic bioventing

Bioremediation Myths

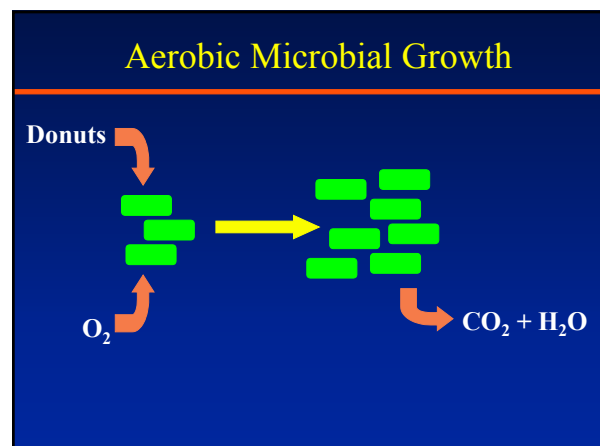
- ♦ Bioremediation is the cheapest remedy – usually but now always!
- ♦ Only dissolved plumes can be treated
- ♦ Volatile organic compounds (VOCs) are toxic to microorganisms at high concentrations
- ♦ Bioaugmentation does not work

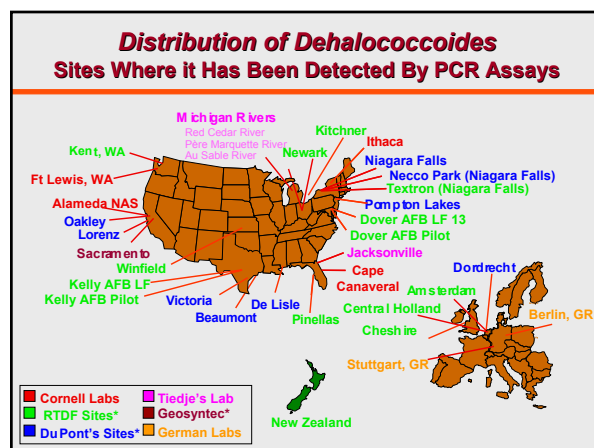
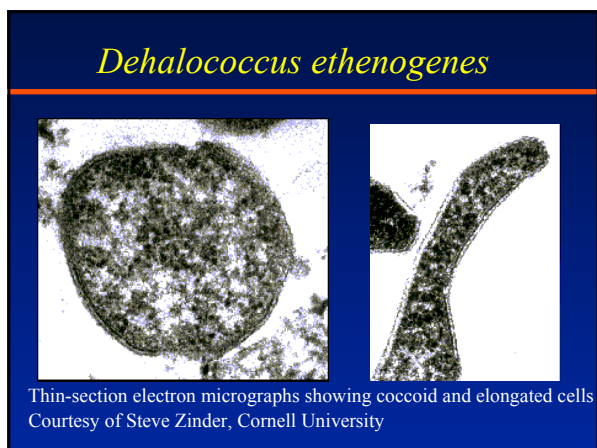
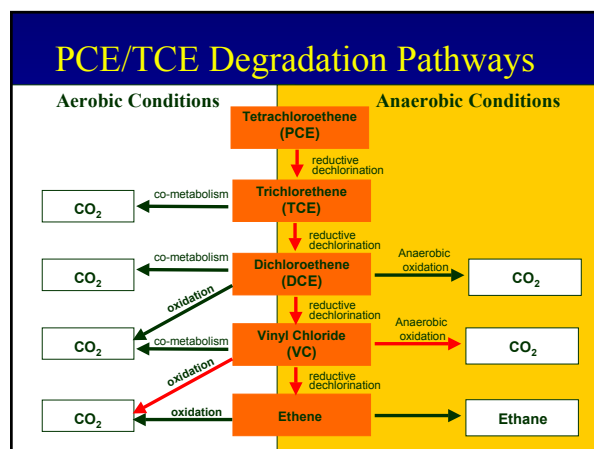
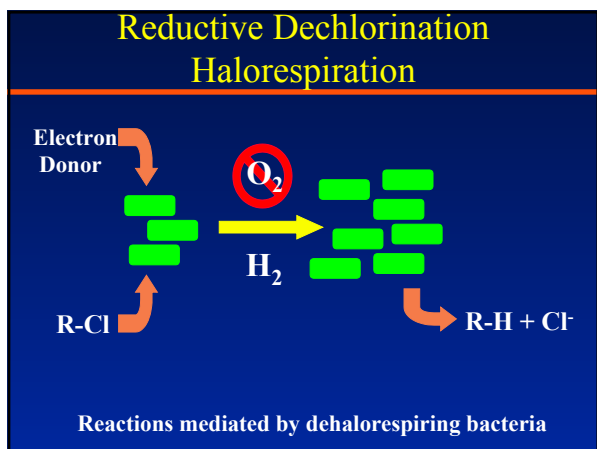
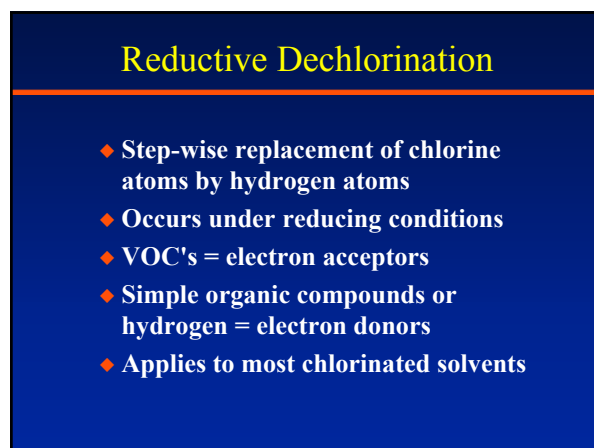
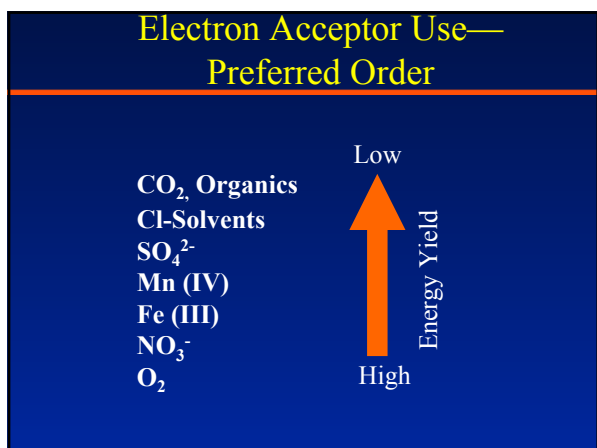


- ### Technology Benefits
- ◆ Treatment is typically in place
 - ◆ Takes advantage of natural processes
 - ◆ Can allow continuing operations
 - ◆ Can be integrated with other technologies
 - ◆ May accelerate source remediation and reduce time to clean up
 - ◆ Accepted by public

- ### Technology Limitations
- ◆ Typically requires nutrient delivery and mixing
 - ◆ Potential for system fouling and associated operation and maintenance (O&M)
 - ◆ Potential to form undesirable degradation intermediates
 - ◆ May not be feasible for large, dilute plumes
 - ◆ Potential for undesirable geochemical changes

- ### Terminology and Definitions
- ◆ **Electron donor**
 - A compound that donates electrons during its oxidation
 - Simple organic compounds such as sugars, alcohols, or methane can be oxidized to carbon dioxide (CO_2)
 - ◆ **Electron acceptor**
 - A compound that accepts electrons during its reduction
 - Inorganic compounds like oxygen, nitrate, sulfate, oxidized metals, or CO_2 can be reduced to water, dinitrogen gas, hydrogen sulfide, dissolved metals, or methane, respectively





Reductive Dechlorination Design Considerations

- ♦ Manipulation of redox conditions
- ♦ Electron donor half-life and hydrogen generation
- ♦ Depletion of competing electron acceptors (e.g., NO_3^- , SO_4^{2-})
- ♦ Potential inhibitors - chloroform, TCA
- ♦ Mass balancing

Reductive Dechlorination Mass Balance Considerations

- ♦ PCE/TCE is typically dechlorinated to ethene
 - Conversion to other products can occur
 - » Methane, ethane, CO_2 , Cl
- ♦ Risk of underestimating system performance based on mass balance calculated on ethene alone

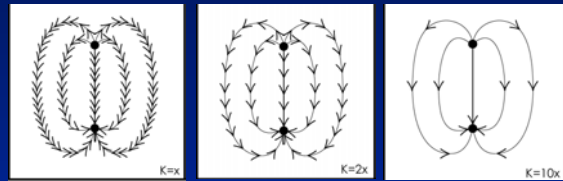
Mass Accounting for Dechlorination Reactions

- Most VOC data presented as micrograms per liter ($\mu\text{g/L}$) or parts per billion (ppb)
- Mass accounting has to be conducted on a molar basis:

$1 \text{ mole TCE} \rightarrow 1 \text{ mole DCE} \rightarrow 1 \text{ mole VC} \rightarrow 1 \text{ mole ethene}$
 $132 \text{ g TCE} \rightarrow 97 \text{ g DCE} \rightarrow 62.5 \text{ g VC} \rightarrow 28 \text{ g ethene}$
- Dechlorination of 132 milligrams per liter of TCE yields only 28 milligrams per liter of ethene

Effect of Hydraulic Conductivity on Nutrient Delivery

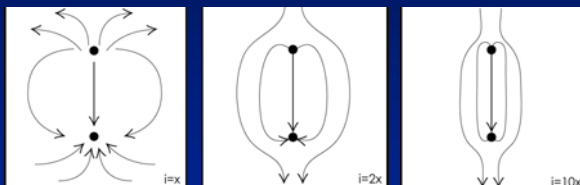
Each arrowhead on the particle track represents one day travel time



Delivery system must balance time to delivery point with half-life of added nutrient and well costs

Effect of Hydraulic Gradient on System Design

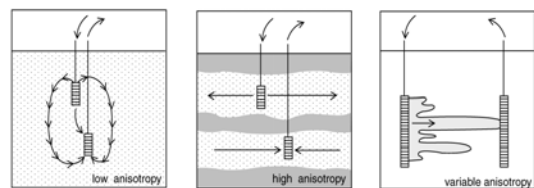
Low gradients can result in poor hydraulic control over nutrient delivery



Strong gradients can limit dispersion of nutrients over target area, requiring more delivery locations

Effect of Anisotropy on System Design

Should nutrient delivery use horizontal or vertical wells?



(High anisotropy can bias nutrient delivery to high K zones)

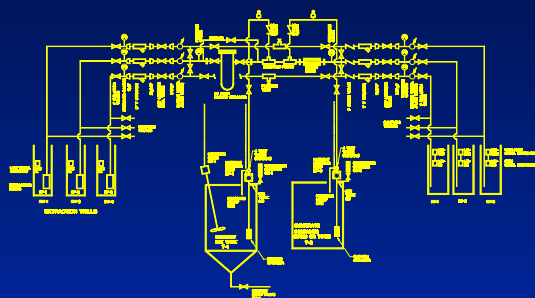
Dover AFB Pilot Test Objectives

- ◆ Design an in situ anaerobic dechlorination pilot for groundwater treatment
- ◆ Demonstrate stimulated degradation of TCE
- ◆ Demonstrate biogenic transformations to non-chlorinated end products
- ◆ Develop performance and cost data

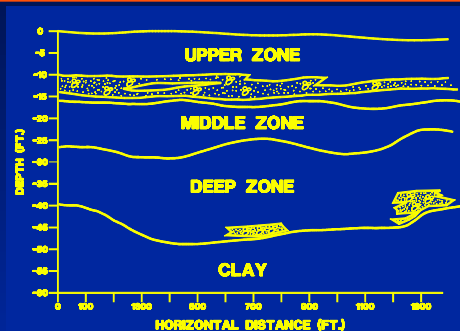
Dover AFB VOC Concentrations

- ◆ PCE 50 ug/l
- ◆ TCE 5,000 - 10,000 ug/l
- ◆ cis-DCE 1,000 - 2,000 ug/l
- ◆ VC 20 ug/l

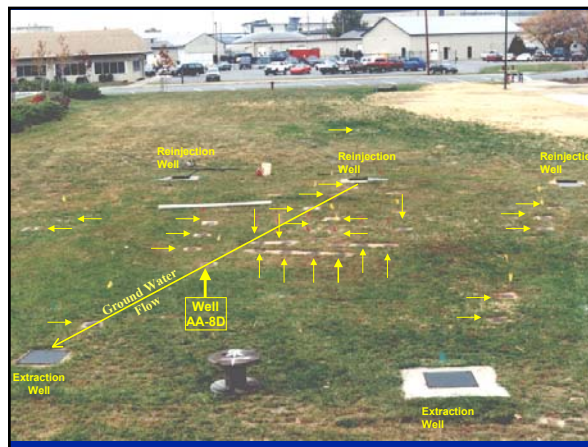
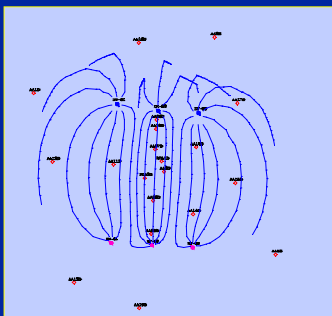
Pilot Design PFD



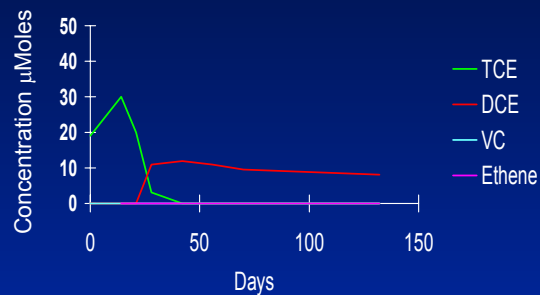
Typical Cross-Section



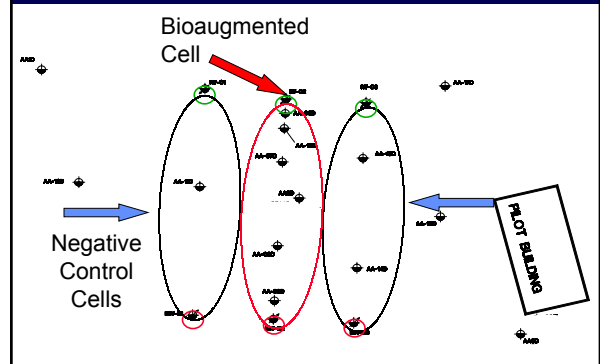
Hydraulically Isolated Treatment Cell



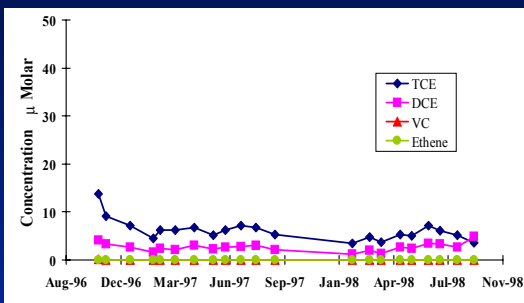
Laboratory Test Results



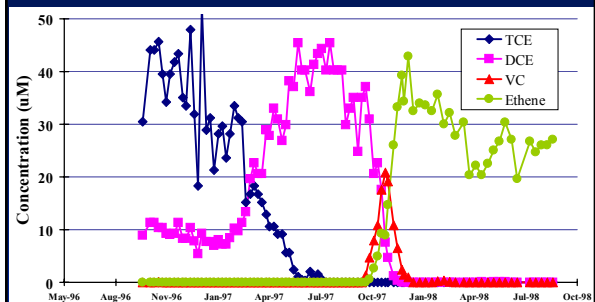
Bioaugmentation vs. Flow Cells



Pilot Results—Well DM-316 (upgradient)



Pilot Results—Well AA-8D



BIOAUGMENTATION TEST RESULTS

- Microcosm studies indicated only partial dehalogenation - to cis-1,2 DCE
- Field studies confirmed the lab work - dechlorination stopped at cis 1,2 DCE
- A 90-day delay before dechlorination of cis-1,2 DCE to VC and ETH was observed
- Complete biodegradation was observed
- US Air Force scaled this up as their remedy
- Bioaugmentation will allow treatment at many other sites where there are no native dechlorinating bacteria

Performance Validation Did It REALLY Work???

- ♦ Criteria differ for each biodegradation mechanism
- ♦ Criteria based on scientific knowledge of the biodegradation process
- ♦ Determine from chemical data
- ♦ Make sure it's not just dilution (or magic)!

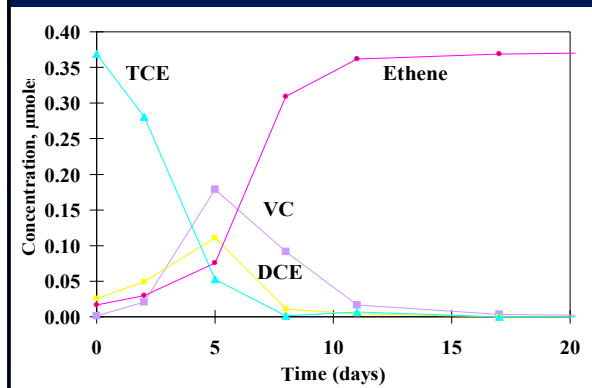
Reductive Dechlorination

- ◆ Mass balance based on chemical analyses
 - Conversion of solvents to ethene or ethane
 - Creation of dissolved chloride
- ◆ The proportions of the various solvents must change over time
- ◆ Compare data on a MOLAR BASIS!!

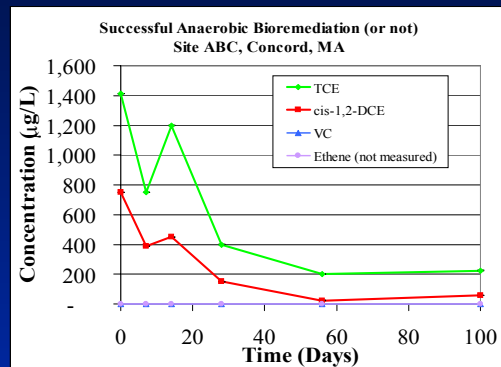
Reductive Dechlorination

- ◆ Data must be compared against tracers
 - If tracer concentrations decline the same as the VOC's, it isn't degradation - it's dilution!
- ◆ Conditions must be (and stay) anaerobic
 - Depletion of electron acceptors (NO_3 , SO_4)
 - Depletion of electron donors
 - No dissolved oxygen, redox below -150 mv
- ◆ Detection of necessary organisms helps

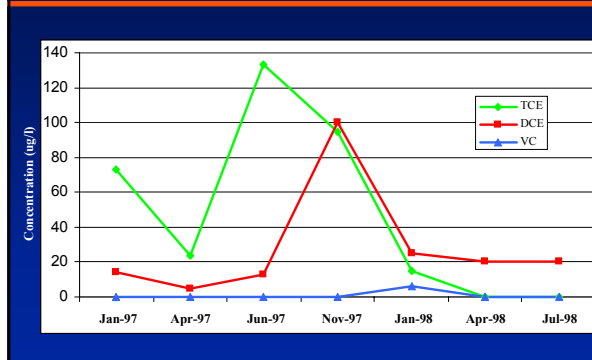
Good Data—Dechlorination



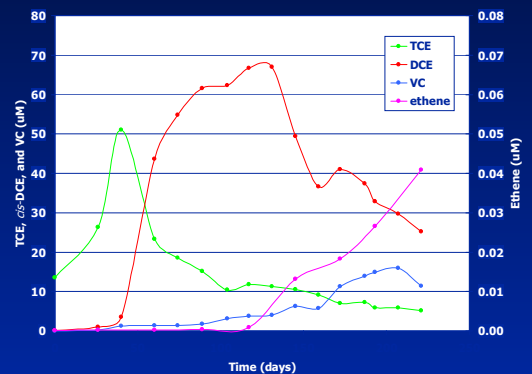
Bad Data that Looks Good



Reduction Dechlorination? 4 Problems



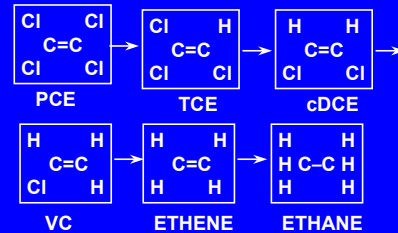
Is There a Problem Here?



USE OF EDIBLE OIL EMULSIONS TO SUPPORT IN SITU REDUCTIVE DECHLORINATION

M. D. LEE
TERRA SYSTEMS, INC.

PCE DECHLORINATION



REDUCTIVE DECHLORINATION REQUIREMENTS

- ★ PRESENCE OF MICROBIAL POPULATION CAPABLE OF COMPLETE DECHLORINATION
- ★ AVAILABILITY OF SUBSTRATE AND NUTRIENTS AND CONTROL OF ELECTRON ACCEPTORS
- ★ FAVORABLE ENVIRONMENTAL CONDITIONS

SUBSTRATE DELIVERY

- ★ SOLUBLE SUBSTRATE
 - ♦ FORCED GRADIENT FROM RECIRCULATION SYSTEM
 - ♦ POTENTIAL FOR PLUGGING
 - ♦ FREQUENT SUBSTRATE REAPPLICATION
- ★ PASSIVE SYSTEM
 - ♦ SOLUBLE SUBSTRATE USING NATURAL GRADIENT
 - ♦ LONG-LASTING SUBSTRATE

LONG-LASTING SUBSTRATES

- ★ HYDROGEN RELEASE COMPOUND (HRC)
- ★ EDIBLE OIL
- ★ EDIBLE OIL EMULSION (EOS™)

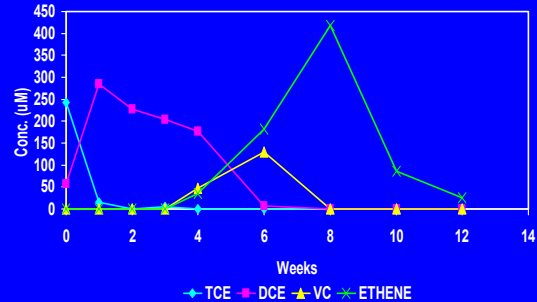
VALUE OF EDIBLE OILS

- ★ INEXPENSIVE (\$2.00-4.00/LB) VERSUS HRC (\$5.00-8.00/LB)
- ★ LONG LASTING (>2 YRS IN FIELD STUDY)
- ★ AVOIDS RECIRCULATION SYSTEM INSTALLATION AND O&M
- ★ CAN BE USED AS BARRIER OR SOURCE TREATMENT

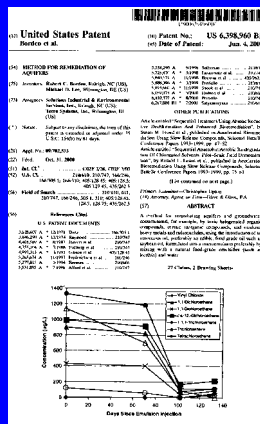
DIRECT INJECTION OF EDIBLE OILS VERSUS EDIBLE OIL EMULSIONS

- ★ DIRECT INJECTION OF OIL
 - ◆ LIMITED DISTRIBUTION
 - ◆ VISCOUS
 - ◆ FLOATS TO SURFACE
- ★ EOS™ INJECTION
 - ◆ BETTER DISTRIBUTION
 - ◆ VISCOSITY SIMILAR TO WATER
 - ◆ DROPLETS IMMOBILIZED

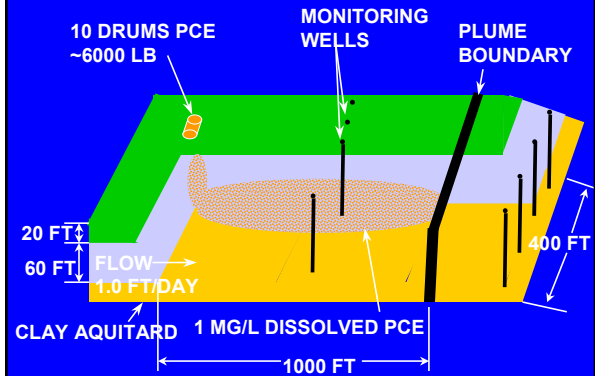
Till with Soybean Oil Plus Yeast Extract and Pinellas Dechlorinating Enrichment



**US PATENT
6,398,960
METHOD FOR
REMEDATION
OF AQUIFERS
R. C. BORDEN
M. D. LEE
JUNE 4, 2002**



SITE REMEDIATION ECONOMICS (QUINTON ET AL. 1997)

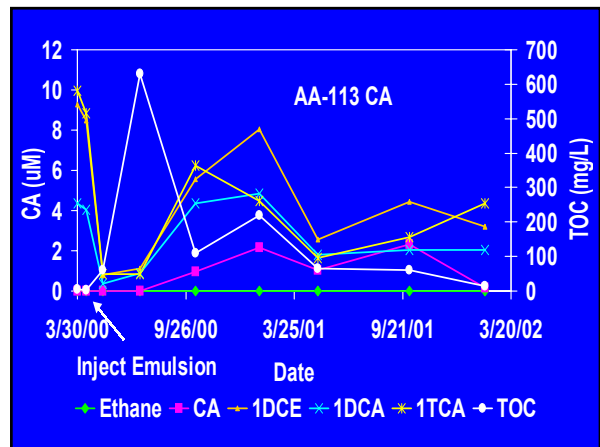
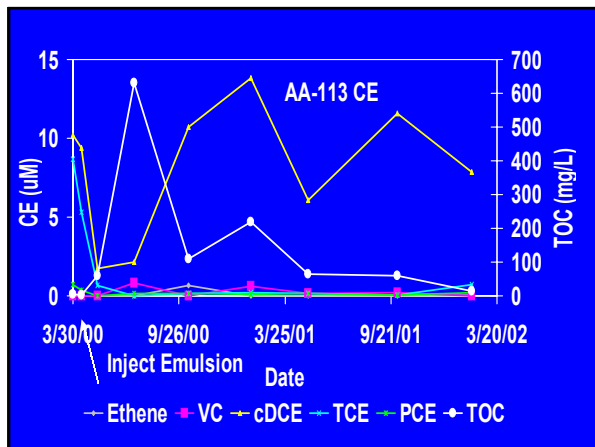
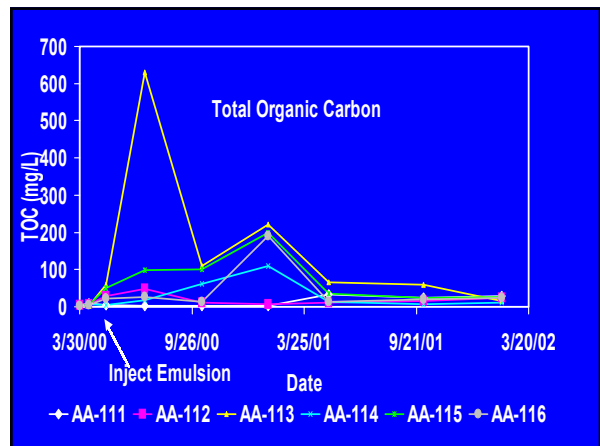
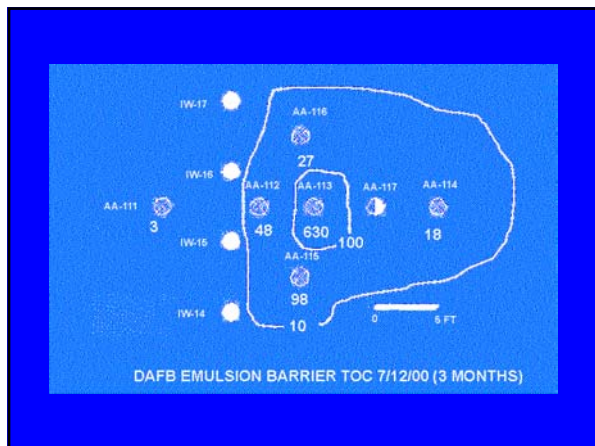


SITE REMEDIATION ECONOMICS

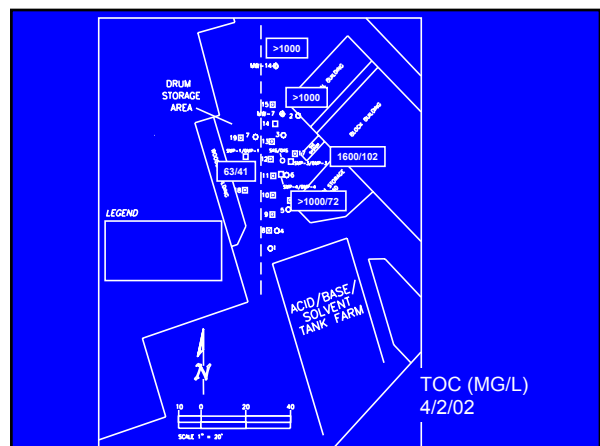
- ★ TEMPLATE SITE WITH 6,000 LBS. OF PCE
 - ◆ PUMP & TREAT \$9.8M
 - ◆ ZVI BARRIER WALL \$3.9M
 - ◆ RECIRCULATING BIO \$1.3M
 - ◆ M.N.A \$0.9M
 - ◆ EOS SYSTEM \$0.8M

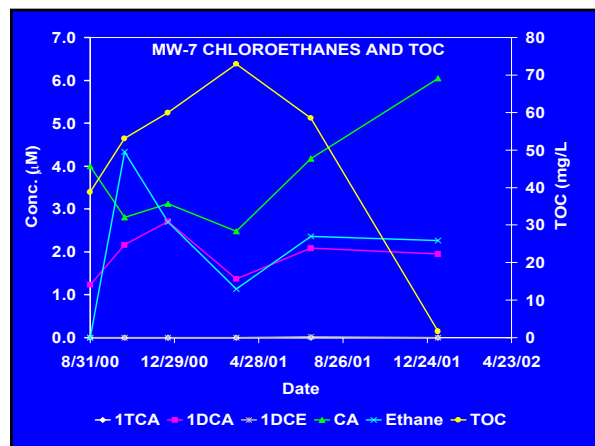
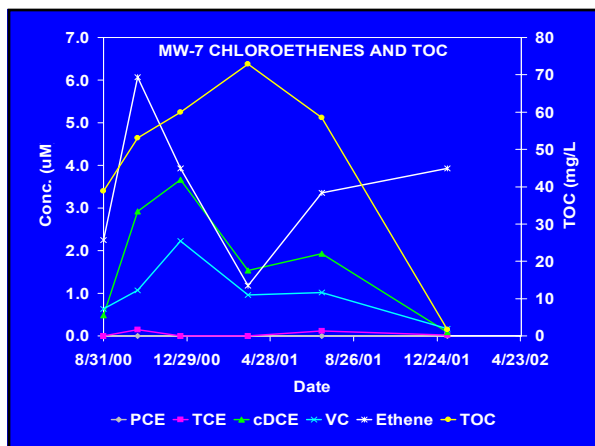
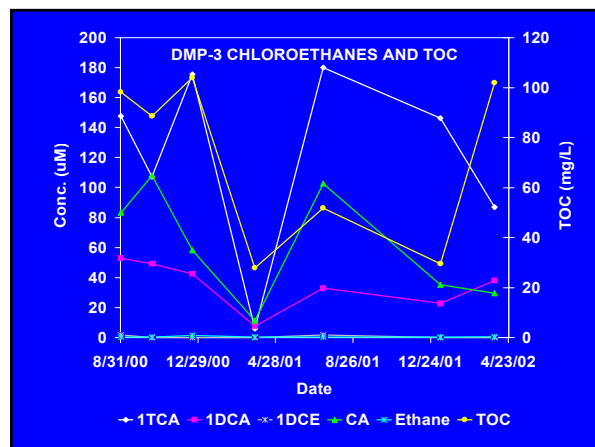
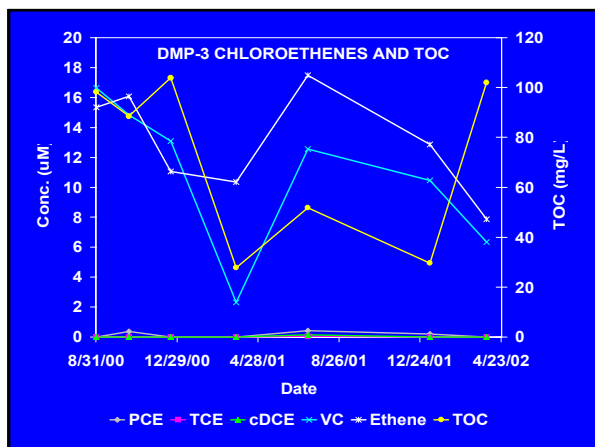
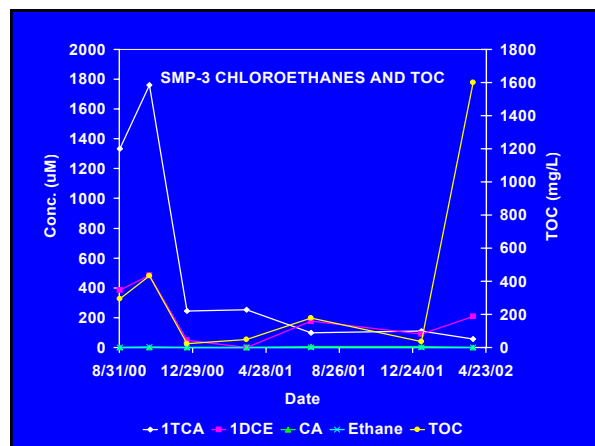
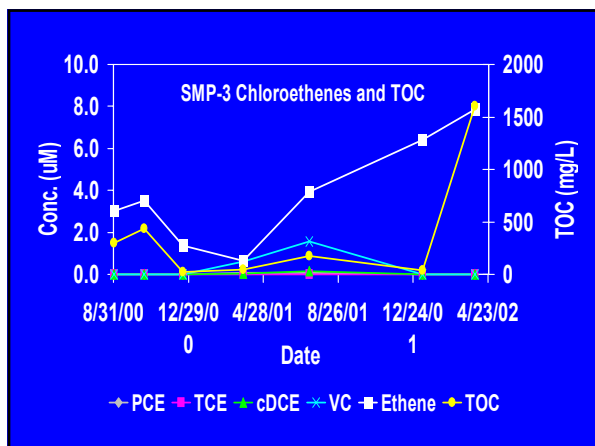
DOVER AFB EMULSION BARRIER PILOT

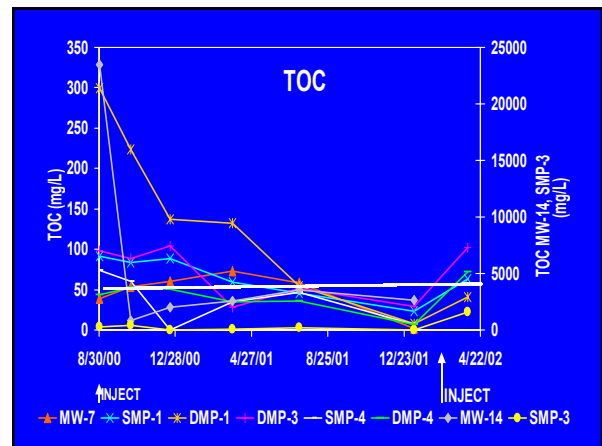
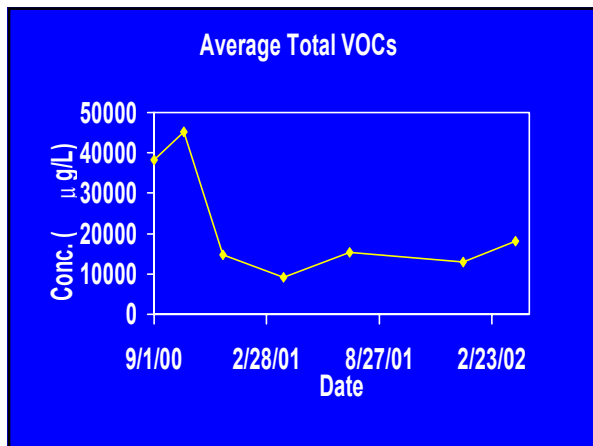
- ★ DOVER AFB PILOT UPGRADIENT OF
RTDF ACCELERATED ANAEROBIC PILOT
- ★ CONTAMINATED WITH PCE, TCE, cDCE,
1TCA, 1DCA, AND 1DCE
- ★ TWO BARRIERS INSTALLED
 - ◆ DIRECT OIL INJECTION
 - ◆ EMULSION



- ### LONG ISLAND EMULSION PILOT
- ★ INDUSTRIAL FACILITY CONTAMINATED WITH 1,1,1-TCA, PCE, DAUGHTER PRODUCTS, AND OTHER ORGANICS
 - ★ INJECTED EMULSION BETWEEN 22 AND 50 FT BGS INTO SIX GEOPROBE POINTS AND OIL INTO ONE POINT
 - ★ EMULSION MOVED AT LEAST 25 FT TO MONITORING WELL
 - ★ SECOND INJECTION EVENT AFTER 17 MONTHS INTO 12 INJECTION WELLS





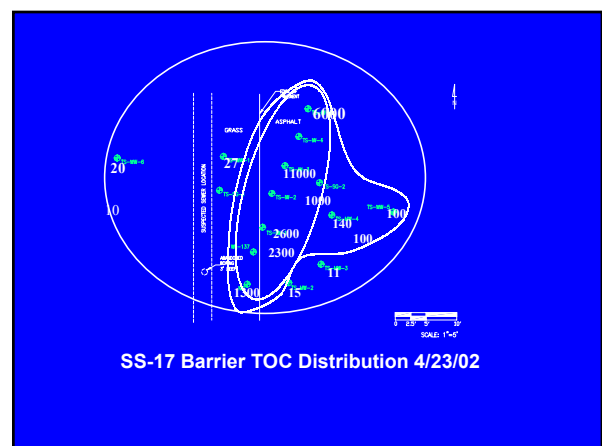
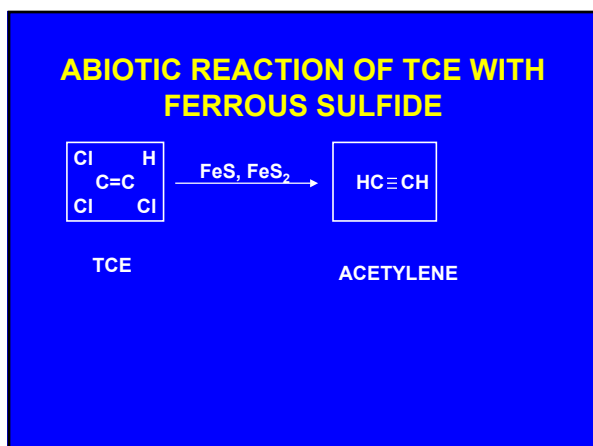


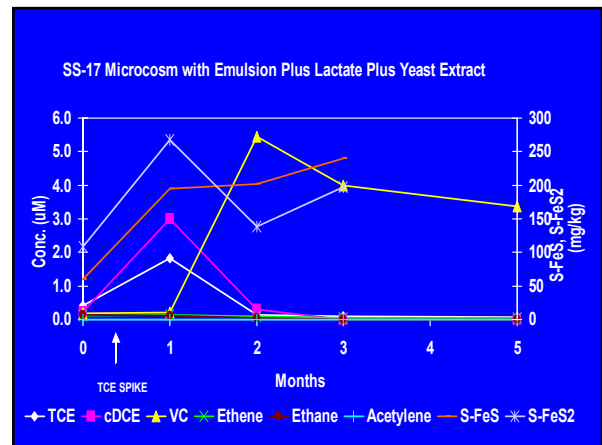
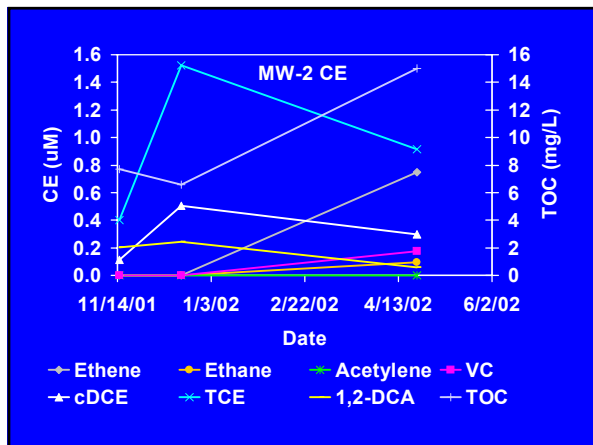
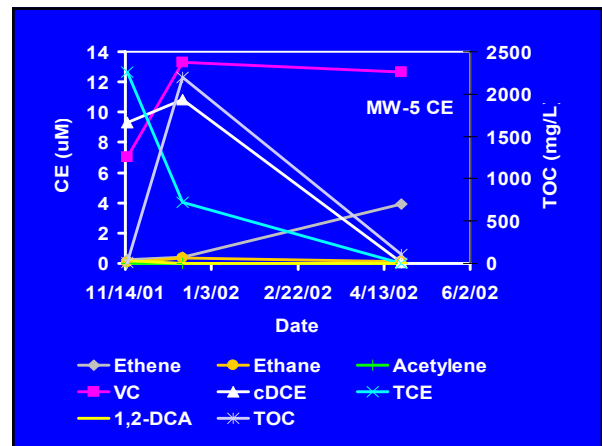
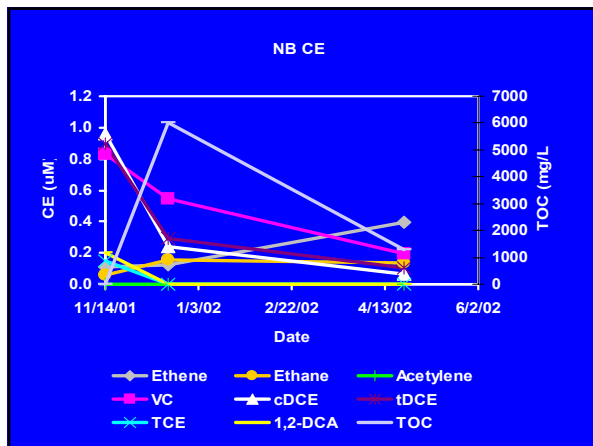
LONG ISLAND SUMMARY

- ★ OVER 52% TOTAL VOLATILES REMOVED
- ★ TOC LEVELS FELL BELOW OPTIMUM AFTER 16 MONTHS
- ★ INJECTED ADDITIONAL EOS MARCH 2002
- ★ GOOD DISTRIBUTION OF EOS
- ★ EOS PROMOTING BIODEGRADATION OF PCE AND 1TCA

ALTUS AFB SS-17 PILOT

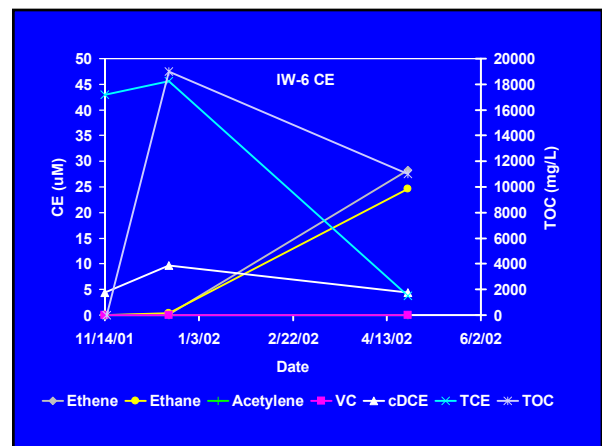
- ★ SS-17 IMPACTED BY HYDROCARBON SPILL; PARTIAL DECHLORINATION OF TCE TO cDCE AND VC
- ★ EOS™ INJECTED INTO 6 INJECTION WELLS IN DECEMBER 2001
- ★ SEVEN MONITORING WELLS AND FOUR INJECTION WELLS SAMPLED 11/01, 12/01 (FOLLOWING EMULSION INJECTION), AND 4/02





ALTUS AFB OU-1 PILOT

- ★ SMALLER SCALE PILOT NEAR LANDFILL CONTAMINATED WITH TCE
- ★ GROUNDWATER CONTAINS ABOUT 1,800 MG/L SULFATE
- ★ INJECTED EOS™ INTO TWO WELLS. WELL IW-7 RECEIVED GROUNDWATER FROM SS-17 BARRIER THOUGHT TO CONTAIN DECHLORINATING POPULATION
- ★ MONITORING TWO INJECTION WELLS, ONE NEARBY WELL, AND ONE DOWNGRAIENT WELL



ALTUS AFB CONCLUSIONS

- ★ EOS™ INJECTION SUPPORTS REDUCTIVE DECHLORINATION OF TCE AND cDCE TO VC, ETHENE, AND ETHANE EVEN UNDER HIGH SULFATE CONDITIONS
- ★ EOS™ MOVED AT LEAST 25 FEET AT SS-17 BARRIER
- ★ WHILE FERROUS SULFIDE AND FERROUS DISULFIDE ARE BEING GENERATED, THEY ARE NOT PROMOTING THE ABIOTIC REACTION YIELDING ACETYLENE

EDIBLE OIL EMULSION CONCLUSIONS

- ★ REDUCES O & M, SUBSTRATE COSTS
- ★ CAN BE EFFECTIVE FOR SOURCE CONTROL OR AS BARRIER
- ★ BETTER DISTRIBUTION THAN DIRECT OIL INJECTION OR HRC
- ★ MAY BE USED IN CONJUNCTION WITH BIOAUGMENTATION

Combined Chemical and Biological Strategies for Remediation of Persistent PAH Contaminants and Their Effects on Biodegradation

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if you would like a copy of the
presentation Slides.